Vibrational spectroscopy of synthetic stercorite $H(NH_4)Na(PO_4)\cdot 4H_2O$ – a comparison with the natural cave mineral

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Abstract

In order to mimic the chemical reactions in cave systems, the analogue of the mineral stercorite $H(NH_4)Na(PO_4)\cdot 4H_2O$ has been synthesised. X-ray diffraction of the stercorite analogue matches the stercorite reference pattern. A comparison is made with the vibrational spectra of synthetic stercorite analogue and the natural Cave mineral. The mineral in nature is formed by the reaction of bat guano chemicals on calcite substrates.

A single Raman band at 920 cm^{-1} (Cave) and 922 cm-1 (synthesised) defines the presence of hydrogen phosphate in the mineral. In the synthetic stercorite analogue, additional bands are observed and are attributed to the dihydrogen and phosphate anions. The vibrational spectra of synthetic stercorite only partly match that of the natural stercorite. It is suggested that natural stercorite is more pure than that of synthesised stercorite. Antisymmetric stretching bands are observed in the infrared spectrum at 1052, 1097, 1135 and 1173 cm^{-1}. Raman spectroscopy shows the stercorite mineral is based upon the hydrogen phosphate anion and not the phosphate anion. Raman and infrared bands are found and assigned to PO_4^{3-}, H_2O,

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OH and NH stretching vibrations. Raman spectroscopy shows the synthetic analogue is similar to the natural mineral. A mechanism for the formation of stercorite is provided.

KEYWORDS: synthesis, stercorite, ‘cave’ mineral, brushite, mundrabillaite, archerite, Raman spectroscopy.

Introduction

Many minerals are formed in cave systems. The reaction of bat guano with calcite surfaces enables these reactions. The calcite surfaces act as sites for nucleation and crystallisation. These minerals are formed through the chemical reactions of calcite with bat guano or with chemicals from bat guano which are water soluble and crystallise out on the calcite surfaces. The mineral stercorite $H(NH_4)Na(PO_4)\cdot 4H_2O$ is water soluble and may translocate through the cave networks such as in the Petrogale cave [1]. As such, many minerals form in these caves and include archerite $(K,NH_4)(H_2PO_4)$ [2] and mundrabillaite $(NH_4)_2Ca(HPO_4)_2\cdot H_2O$ [3]. These minerals occur as stalactites and as crusts on the walls and floors of the caves. Other minerals found in the Petrogale cave include aphthitalite $(K,Na)_3Na(SO_4)_2$, halite NaCl, syngenite $(K,Na)_3Na(SO_4)_2$, oxammite $(NH_4)_2(C_2O_4)\cdot H_2O$, weddellite $Ca(C_2O_4)\cdot 2H_2O$, whitlockite $Ca_9Mg(PO_4)_6(HPO_4)$, guanine $C_5H_5N_5O$, newberyite $Mg(HPO_4)\cdot 3H_2O$ and calcite $CaCO_3$. The objective of this research is to mimic the chemical reactions that occur in caves and thus form the analogue of stercorite. Then, a comparison of the vibrational spectra of the analogue with that of the natural mineral will be made.

The name ‘stercorite’ is derived from the Latin word for ‘dung’. Stercorite is a triclinic mineral (pseudomonoclinic) [4] and is whitish to yellow in colour. This mineral belongs to space group 1bar with cell dimensions a = 10.636(2), b = 6.9187(14), c = 6.4359(13), α = 90.46(3), β = 97.87(3),γ = 109.20(3) with Z = 2 [4]. The mineral is congruent with respect to its components. Stercorite has a (100) layered structure built up by [010] rows of Na octahedra sandwiched between P tetrahedra; NH_4^+ and equivalent water molecules with tetrahedral environments, intercalate the layers and link them through H bonds [4]. The solubility and phase equilibrium diagram has been published [1].

The amount of published data on the Raman spectra of mineral phosphates is limited [5-9]. Further, there is almost no data on the Raman or infrared spectroscopy of the phosphate ‘cave’ minerals. The Raman spectra of the hydrated hydroxy phosphate minerals have been reported only to a limited extent. In aqueous systems, Raman spectra of phosphate oxyanions show a symmetric stretching mode (ν_1) at 938 cm^{-1}, the antisymmetric stretching mode (ν_3) at

1017 cm^{-1}, the symmetric bending mode (ν_2) at 420 cm^{-1} and the ν_4 bending mode at 567 cm^{-1} [7, 8, 10]. More recent values have been reported by Rudolph and Irmer [11]. Density functional calculations enabled more precise measurements of the positions of the phosphate vibrational modes [11].

Raman spectroscopy has proven most useful for the study of mineral structure [12-35]. The detailed comparative study of the vibrational spectra of the synthetic analogue and the natural stercorite cave mineral has not been published. The objective of this research is to report the Raman and infrared spectra of synthetic stercorite and to relate the spectra to the mineral structure.

Experimental

Synthesis of the analogue of stercorite

The chemicals were purchased as follows: sodium phosphate dibasic from Sigma-Aldrich and ammonium phosphate dibasic from BDH Laboratory Supplies. 25.90g Na_2HPO_4 was dissolved in 500 ml of deionized water. With stirring 24.30g $(NH_4)_2HPO_4$ was slowly added into disodium hydrogen phosphate solution. Concentration of the mixture solution was achieved by evaporation. The resulted gelatinous-like product was dried in oven for 20 hours. XRD showed the stercorite analogue was stercorite.

Mineral

The mineral stercorite was supplied by The Australian Museum and originated from Petrogale Cave, Madura, Western Australia (museum sample number D54069). Details of the mineral have been published (page 561) [36]. The mineral corresponds to the formula $H(NH_4)Na(PO_4)\cdot 4H_2O$.

Raman spectroscopy

Crystals of stercorite or its synthetic analogue were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarised

light at 633 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of ± 1 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition on the crystals using the highest magnification (50x) was accumulated to improve the signal to noise ratio in the spectra. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-addition of 128 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio. The infrared spectra are shown in the supplementary information.

Band component analysis was undertaken using the Jandel 'Peakfit' (Erkrath, Germany) software package which enabled the type of fitting function to be selected and allowed specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Lorentz-Gauss ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations (r^2) greater than 0.995. Band fitting of the spectra is quite reliable providing there is some band separation or changes in the spectral profile.

RESULTS AND DISCUSSION

Background

S.D. Ross in Farmer (1974) (page 404) listed some well-known minerals containing phosphate, which were either hydrated or hydroxylated or both [37]. The value for the ν_1 symmetric stretching vibration of PO_4 units was given as 930 cm^{-1} (augelite), 940 cm^{-1} (wavellite), 970 cm^{-1} (rockbridgeite), 995 cm^{-1} (dufrenite) and 965 cm^{-1} (beraunite). The position of the symmetric stretching vibration is mineral dependent and a function of the cation and crystal structure. The fact that the symmetric stretching mode is observed in the infrared spectrum affirms a reduction in symmetry of the PO_4^{3-} units. This reduction in symmetry can be caused by site symmetry and/or factor group splitting.

X-ray diffraction

The X-ray diffraction pattern of the synthesised stercorite analogue is shown in Figure 1. The pattern matches the standard reference pattern. These matching patterns prove that the synthesised stercorite analogue is indeed stercorite.

Spectroscopy

The Raman spectrum of the synthesised analogue over the 100 to 4000 cm^{-1} range and the infrared spectrum of the synthesised analogue over the 500 to 4000 cm^{-1} range are shown in Figures S1 and S2 . These spectra are then divided into sections according to the particular vibrations for example Figure 2 shows the region of the symmetric stretching vibration and Figure 3 displays the bending modes. Figure 4 shows the OH stretching region.

The Raman spectra of synthetic stercorite and natural stercorite from Petrogale Cave, Madura, Western Australia in the 650 to 1250 cm^{-1} region are displayed in Figures 2a and 2b. The corresponding infrared spectra in the 500 to 1350 cm^{-1} region are shown in the supplementary information as Figures S3a and S3b. The Raman spectra are dominated by an intense band at 920 cm^{-1} assigned to the ν_1 HPO_4^{3-} symmetric stretching mode. The observation of a single band for natural stercorite is perhaps unexpected, as with three different cations in the mineral structure, it might be expected that the band would split into component bands. Further, the single band observed in the Raman spectrum suggests that the symmetry of the phosphate anion is preserved in the mineral structure. In addition, the presence of the proton might suggest the existence of HPO_4^{2-} ions. If this is the case, then again two symmetric phosphate stretching modes would be observed. This is not the case. However, for the synthetic analogue of stercorite, additional phosphate stretching bands are observed at 880 and 962 cm^{-1}. The 880 cm^{-1} band may be assigned to the HPO_4^{2-} stretching vibration. Ross in Farmer [37] (Table 17.IX) detailed the results of the vibrational spectra of hydrogen phosphate compounds, and defined the band at around 880 cm^{-1} to the symmetric stretching vibrations of $P(OH)_2$ units. The band for the aqueous $H_2PO_4^{2-}$ is observed at 878 cm^{-1}. The Raman band at 962 cm^{-1} is assigned to the PO_4^{3-} symmetric stretching mode. Ross lists the band positions for many natural minerals in Table 17.X [37]. Many of these minerals

have bands at around 962 cm^{-1}. Natural stercorite appears more pure than the synthetisised stercorite analogue.

In the infrared spectrum of stercorite analogue a sharp absorption band is observed at 881 cm^{-1}. This band is the infrared equivalent of the Raman band at 880 cm^{-1}. The band is of low intensity in the infrared spectrum of natural stercorite and is observed at 871 cm^{-1}. The sharp infrared band of the synthetic analogue shows a sharp band at 995 cm^{-1} attributed to the PO_4^{3-} symmetric stretching vibration. Infrared bands at 1064, 1149 and 1176 cm^{-1} are assigned to the phosphate antisymmetric stretching bands. The bands observed at 1245 and 1280 cm^{-1} are due to the OH in-plane bend. An intense infrared band for natural stercorite is found at 1097 cm^{-1} with component bands at 1052, 1135 and 1173 cm^{-1}. These bands are attributed to phosphate antisymmetric stretching modes. Raman bands in these positions were not observed. It is not possible to distinguish whether the bands are assigned to the dihydrogen phosphate, the monohydrogen phosphate or the phosphate anions. Some of the infrared bands at 695, 726 and 837 cm^{-1} for the stercorite analogue and 674, 755 and 773 cm^{-1} may be attributed to water librational modes. Ross reported infrared bands in these positions but did not assign the bands [37]. Galy [38] first studied the polarized Raman spectra of the $H_2PO_4^-$ anion. Choi *et al.* reported the polarization spectra of NaH_2PO_4 crystals. Casciani and Condrate [39] published spectra on brushite and monetite together with synthetic anhydrous monocalcium phosphate ($Ca(H_2PO_4)_2$), monocalcium dihydrogen phosphate hydrate ($Ca(H_2PO_4)_2 \cdot H_2O$) and octacalcium phosphate ($Ca_8H_2(PO_4)_6 \cdot 5H_2O$). These authors determined band assignments for $Ca(H_2PO_4)$ and reported bands at 1002 and 1011 cm^{-1} as POH and PO stretching vibrations, respectively. Casciani and Condrate [39] tabulated Raman bands at 1132 and 1155 cm^{-1} and assigned these bands to P-O symmetric and the P-O antisymmetric stretching vibrations.

The Raman spectrum in the 100 to 650 cm^{-1} region of stercorite analogue and the natural mineral are displayed in Figures 3a and 3b. For the natural stercorite, two Raman bands are resolved at 450 and 476 cm^{-1} and are attributed to the PO_4^{3-} ν_2 bending mode. The observation of two bands suggests some distortion of the phosphate anion, perhaps brought about by the position of the different cations around the phosphate anion. The bands are not observed in the infrared spectrum as the position of the bands lies below the detection limit of

the instrumentation. These Raman bands are also of low intensity for synthetic stercorite analogue (445, 462 and 476 cm^{-1}). The two ν_2 infrared bands for pseudomalachite published by Ross in Farmer [37] were reported at 450 and 422 cm^{-1}. For pseudomalachite Raman bands were observed at 482 and 452 cm^{-1} with equal intensity. Cornetite Raman spectrum showed an intense band at 433 cm^{-1} with minor components at 463 and 411 cm^{-1}. Ross in Farmer [37] reported two bands at 464 and 411 cm^{-1} for cornetite. According to Ross some of the bands attributable to the ν_2 mode can occur for selected phosphates at quite low wavenumbers. For example, the band is at 341 cm^{-1} for $Mg_3(PO_4)_2 \cdot 4H_2O$ and at 317 and 372 cm^{-1} for $Mn_3(PO_4)_2 \cdot 4H_2O$, Thus, the two bands for the stercorite analogue at 341 and 395 cm^{-1} are due to the ν_2 mode. The equivalent bands for natural stercorite occur at 326 and 345 cm^{-1}. Sharp Raman bands are observed at 533 and 562 cm^{-1} for the stercorite analogue. These bands may be attributed to the ν_4 modes. Only a single band for the natural stercorite at 577 cm^{-1} is observed.

The Raman spectra of the stercorite analogue and the natural sample in the 2600 to 3600 cm^{-1} region are displayed in Figures 4 a and 4b. A broad spectral profile is found which may be resolved into component bands. This spectral profile includes the NH stretching vibrations as well as the water hydroxyl stretching bands. For stercorite analogue, the lower wavenumber bands at 2722, 2768 and 2882 cm^{-1} may be assigned to the NH_4 units and the higher wavenumber bands to water stretching bands. For the natural stercorite, the band at 2900 cm^{-1} is attributed to the NH stretching vibration and the two bands at 3024 and 3158 cm^{-1} to the water stretching modes.

The infrared spectra of stercorite analogue and the natural sample are shown in Figures S4a and S4b. For natural stercorite, infrared bands are observed at 3066, 3232 and 3340 cm^{-1}. The infrared spectrum of the synthetic analogue shows complexity with component bands resolved at 2702, 2854, 3022, 3241 and 3389 cm^{-1}. Again these spectral profiles are composed of the bands assignable to the NH and OH stretching vibrations. The infrared spectra of the stercorite analogue and the natural sample in the 1350 to 1850 cm^{-1} region are shown in Figures S5a and S5b.

The stercorite analogue displays a set of overlapping infrared bands at 1661, 1693 and 1751 cm^{-1}. Intense bands are also found at 1407 and 1446 cm^{-1} with a shoulder at 1466 and 1487 cm^{-1}. These bands are attributed to water HOH and ammonium HNH bending modes. The infrared peak centred upon 1631 cm^{-1} for the natural sample is complex and a series of overlapping bands may be resolved. These bands are attributed to water HOH and ammonium HNH bending modes. The infrared bands at 1260, 1318 , 1405 and 1443 cm^{-1} are attributed to NH_4^+ vibrations. Farmer [37] tabulated NH_4^+ vibrations in the 1410 to 1475 cm^{-1} range for ammoniated divalent phosphates (Table 17. XV) and defined these bands as NH_4^+ ν_4 bending modes.

Mechanism of formation of stercorite

In the laboratory, the mineral is readily synthesised by mixing aqueous solutions of sodium hydrogen phosphate Na_2HPO_4 and ammonium hydrogen phosphate $(NH_4)_2HPO_4$ [1]. Platford [1] showed that the two chemicals were in congruency with their components. It is likely that low temperatures aid the formation of stercorite, as might occur in caves on the Nullarbor Plains in Western Australia. Whether or not the mineral stercorite is formed by simple solubility effects from undersaturated solutions is open to question, but it does seem likely. The presence of the calcite surface serves as a surface for the crystallisation of stercorite. The following reaction is envisaged:

$$Na_2HPO_4 + (NH_4)_2HPO_4 + 5H_2O \rightarrow H(NH_4)Na(PO_4)\cdot 4H_2O + NaOH$$

In order to test this reaction we synthesised the stercorite analogue to prove the above reaction's validity. In our synthesis the stercorite analogue, based upon the Raman spectra, appears to contain phosphate units as well as hydrogen phosphate units.

CONCLUSIONS

The mineral stercorite is an ammoniated hydrogen sodium phosphate and is found in caves in Western Australia and is especially known from the Petrogale Cave, near Madura, Western Australia. The mineral has been found in the Jenolan Caves (Australia). It is a mineral formed by the reaction of calcite with bat (or bird) guano. The mineral is associated with

other phosphate minerals including struvite, archerite, brushite. According to Platford [1], the mineral is formed from solution. Hence the basic components of the mineral can be translocated through a cave system.

In order to test the formation of stercorite in the cave minerals we have synthesised the analogue of stercorite. X-ray diffraction proves that the stercorite analogue was synthesised. A comparison is made with the vibrational spectrum of the stercorite analogue and the natural Cave mineral. The mineral because of the individual vibrating units, lends itself to vibrational spectroscopy. A combination of Raman and infrared spectroscopy has been used to identify vibrational modes associated with the Cave mineral stercorite and the synthetic analogue. The question arises as to whether the mineral contains hydrogen phosphate units or simply phosphate units. Based upon Raman spectroscopy, the anion in the mineral stercorite is the hydrogen phosphate anion and no observation of phosphate units were found. However for the synthetic stercorite analogue Raman bands are attributable to both hydrogen phosphate and phosphate units.

Acknowledgments

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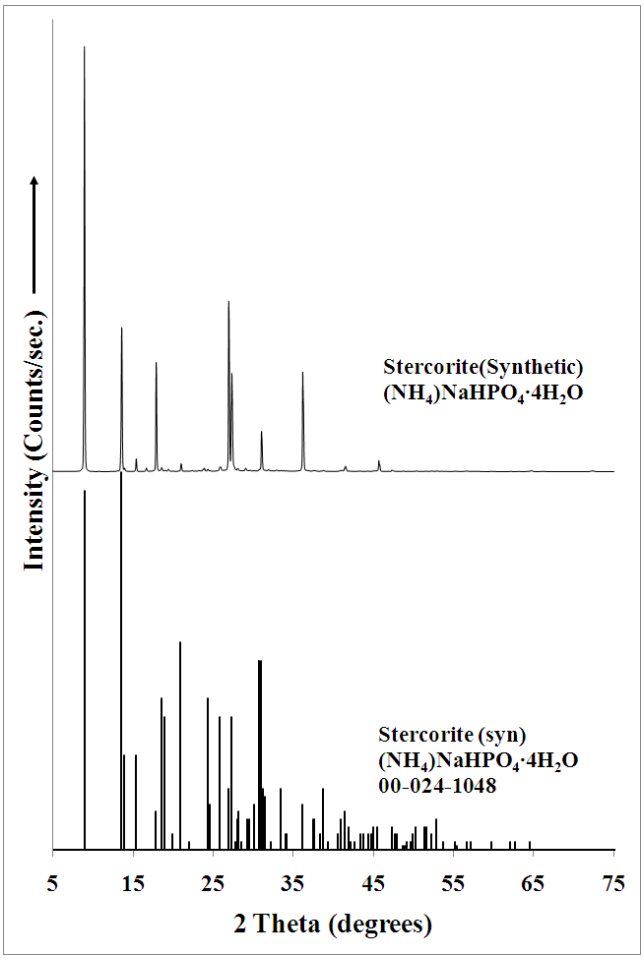
List of Figures



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338 **Figure 1**

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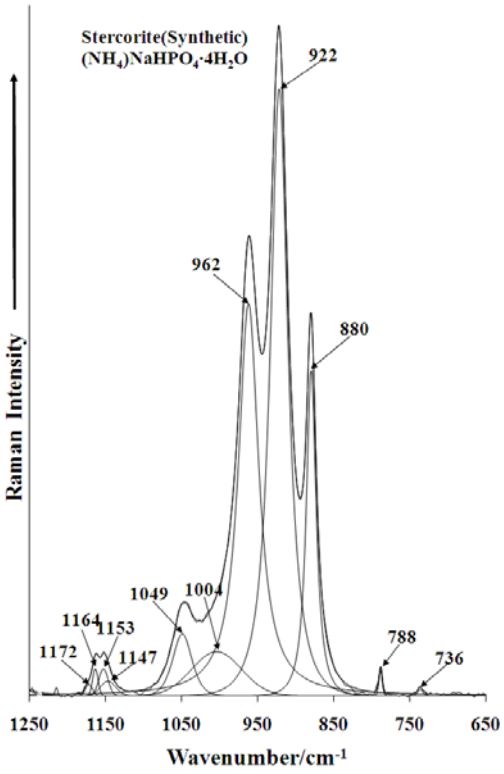

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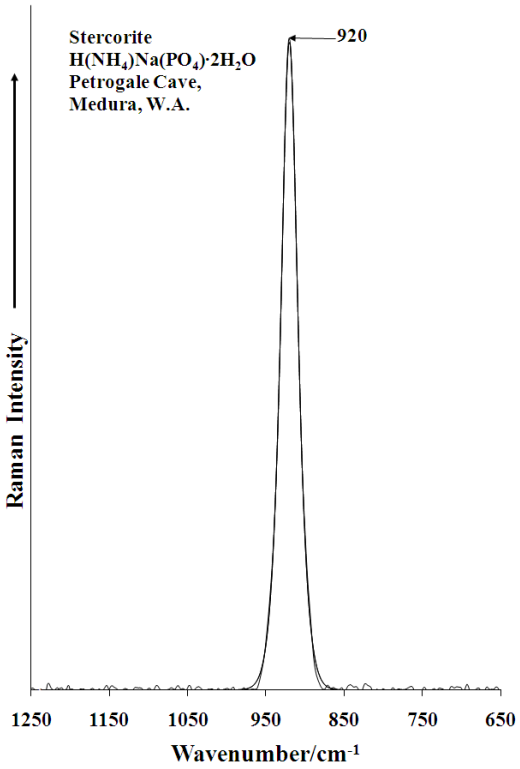

Figure 2b

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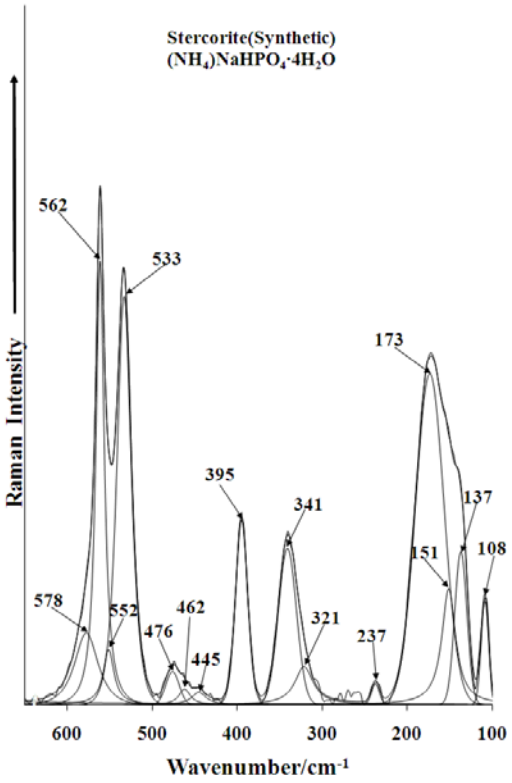

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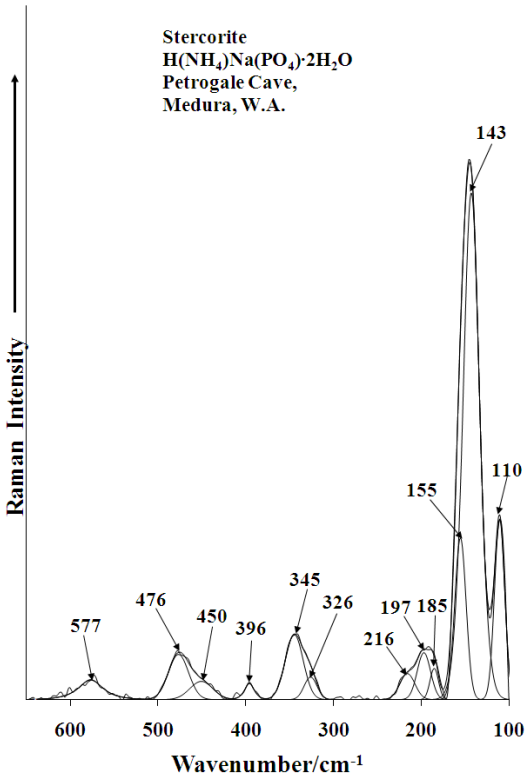

Figure 3b

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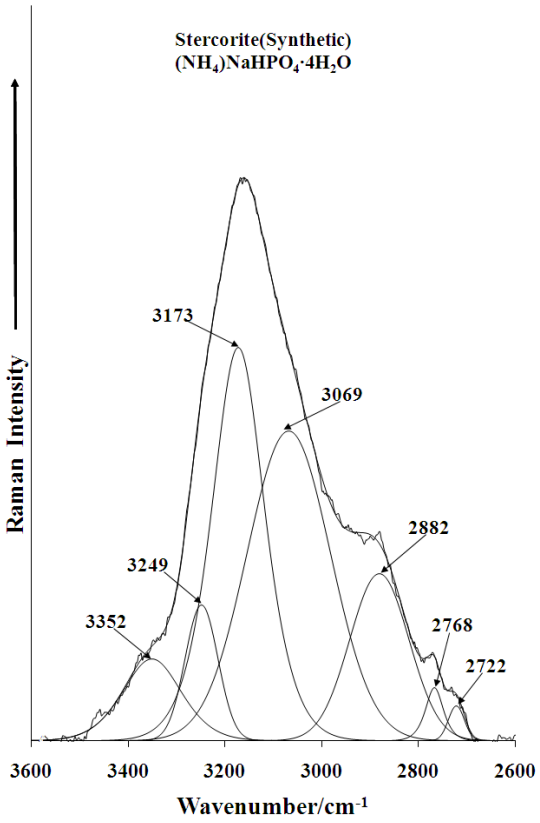

Figure 4a

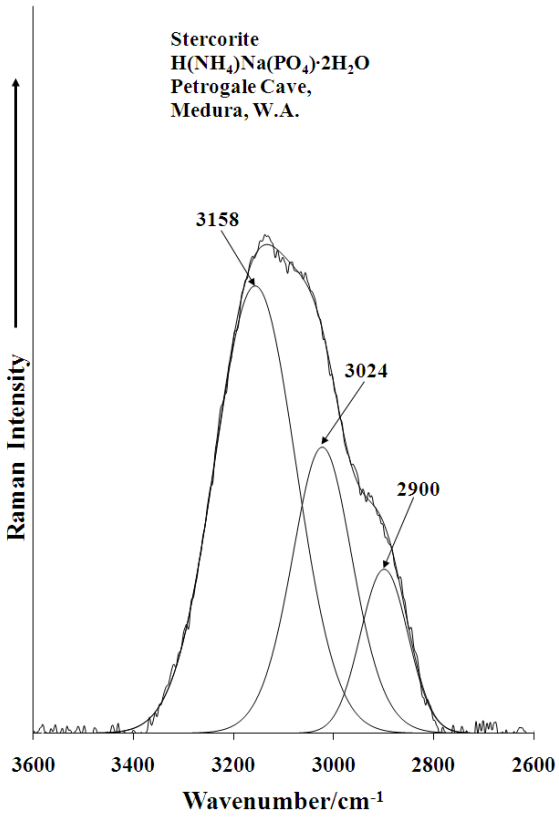

Figure 4b

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